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AT/2813

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE
BEFORE THE BOARD OF PATENT APPEALS AND INTERFERENCES

APPELLANTS' MAIN BRIEF ON APPEAL

APPELLANTS: Fumihiko Nakamura et al. ATTORNEY DOCKET NO: 09792909-5122

SERIAL NO.: 09/925,153

GROUP ART UNIT: 2813

FILING DATE: August 8, 2001

EXAMINER: D. Blum

INVENTION: "INSULATING NITRIDE LAYER AND PROCESS FOR ITS
FORMING, AND SEMICONDUCTOR DEVICE AND PROCESS FOR
ITS PRODUCTION"

Hon. Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

SIR:

Appellants submit herewith, in triplicate, Appellants' Main Brief on Appeal under 37 C.F.R. §1.192 in support of the Notice of Appeal mailed on November 21, 2003. The Commissioner is hereby authorized to charge the amount of \$330.00 for the requisite filing fee for filing the Main Brief on Appeal to the Appellants' Attorneys' credit card. Form 2038 is attached.

Appellants petition the Commissioner for Patents to extend this time for filing the Main Brief on Appeal for one month so that the period to file the brief is extended to February 21, 2004. A Postal Money Order No. 03504299760 in the amount of \$110.00 is enclosed to cover the cost of the extension fee.

The Commissioner is hereby authorized to charge any deficiency in fees associated with this communication or credit any overpayment to Deposit Account No. 19-3140. A duplicate copy of this sheet is enclosed.

02/27/2004 JADD01 00000067 193140 09925153

01 FC:1251 110.00 OP
02 FC:1402 330.00 DA

Respectfully Submitted,

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CERTIFICATE OF MAILING

I hereby certify that this original and two copies of this correspondence is being deposited with the United States Postal Service as First Class Mail in an envelope addressed to Mail Stop Appeal Brief-Patents, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450 on February 23, 2004.

Christopher P. Rauch (Reg. No. 45,034)
Christopher P. Rauch



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ITS PRODUCTION"

Hon. Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450

SIR:

In accordance with the provisions of 37 C.F.R. §1.192, Appellants submit this Main Brief on Appeal in support of the Appeal of the above-referenced application.

I. REAL PARTY IN INTEREST:

The real party in interest in the present appeal is the Assignee, Sony Corporation, a Japanese Corporation. The assignment was recorded in the U.S. Patent and Trademark Office at Reel 012627, Frame 0787.

II. RELATED APPEALS AND INTERFERENCES:

There are no related appeals and no related interferences.

III. STATUS OF CLAIMS:

Claims 1, 2, 4-16 and 18-27 are pending in the application. Claims 6-12 and 20-27 are withdrawn from consideration as being directed to a non-elected invention. Claims 3 and 17 have been canceled. The present appeal is directed to claims 1, 2, 4, 5, 13-16, 18 and 19, which were finally rejected in an Office Action dated August 21, 2003. A copy of the non-canceled claims 1, 2, 4-16 and 18-27 is appended hereto as Appendix A.

The status of the claims on appeal is as follows:

Claims 1, 2, 4, 5, 13-16, 18 and 19 are rejected under 35 U.S.C. §102(b) as being anticipated by *Toshiyuki* (JP 10-424586).

IV. STATUS OF AMENDMENTS:

All amendments have been entered in this application.

Appellants note that, in the Office Action Summary of the Office Action of August 21, 2003, the Examiner mistakenly checked box 10(b) indicating that the drawings filed on August 8, 2001 are objected to by the Examiner. Appellants submit that box 10(b) was checked in error, and instead box 10(a) should have been checked to indicated that the drawings are not objected to. The Examiner correctly states on page 2 of the Office Action that the drawings have been accepted.

V. SUMMARY OF THE INVENTION:

This application relates to an insulating nitride layer and to a semiconductor device having an insulating nitride layer. Specifically, the insulating nitride layer is formed as a buffer layer, such as a buffer layer in a semiconductor device, from a III-V nitride compound semiconductor heavily doped mostly with cadmium. (Page 1, lines 5-11; claims 1 and 13).

Referring to Appellants' Figure 1 as an illustrative example, Figure 1 shows an insulating nitride layer 3c formed as a buffer layer in a semiconductor device. In the illustrative example of Figure 1, the insulating nitride layer 3c is formed from gallium nitride (GaN), which is a nitride based semiconductor. The illustrative insulating nitride layer is heavily doped mostly with zinc (Zn), however, in Appellants' claims, the insulating nitride layer 3c is heavily doped mostly with cadmium (Cd). (Page 12, Table 1).

Since the insulating nitride layer 3c is heavily doped mostly with cadmium, the insulating nitride layer 3c has a sufficiently high resistance regardless of the level of undoping by carriers contained in the insulating nitride layer 3c. (Page 10, lines 4-10). For example, the insulating

nitride layer 3c can be doped in an amount not less than $1 \times 10^{17}/\text{cm}^3$. (Page 10, lines 4-10; claims 4 and 18).

As described in Appellants' specification, conventional buffer layers are typically doped with magnesium. (Page 2, lines 1-15). However, when a magnesium-doped buffer layer is located next to an active layer, the magnesium tends to enter the active layer through a process called autodoping. The autodoping of the active layer with magnesium decreases the conductivity of the active layer. (Page 2, lines 1-15). The magnesium also decreases the carrier concentration and mobility in the active layer. (Page 4, lines 2-8). A conventional approach to avoiding these known detrimental effects caused by a magnesium-doped buffer layer, was to use an undoped (*i.e.*, no magnesium) nitride based buffer layer, however that conventional approach resulted in poor insulating performance. (Page 4, line 17- page 5, line 3).

Appellants' claimed insulating nitride layer 3c overcomes those known buffer layer problems because the claimed insulating nitride layer 3c is heavily doped mostly with cadmium. Referring to the illustrative example of Figure 1, an illustrative insulating nitride layer 3c (a buffer layer) is formed between an undoped buffer layer 2 and an undoped active layer 4. An advantage of this structure is that the cadmium doped insulating nitride layer 3c located next to the active layer 4 has a sufficiently high resistance to isolate elements formed on the substrate 1. Also, the claimed insulating nitride layer 3c, which is heavily doped mostly with cadmium, protects the active layer 4 from autodoping with an impurity. (Page 13, lines 6-13). That is, the active layer 4 is not autodoped with cadmium from the insulating nitride layer 3c. Further, the claimed insulating nitride layer 3c assists the active layer 4 with keeping its conductivity. (Page 13, lines 6-13).

Thus, Appellants' claimed insulating nitride layer that is formed as a buffer layer effects unexpected and improved characteristics in a semiconductor device.

VI. ISSUES:

The issue on Appeal is as follows:

Whether the subject matter of claims 1, 2, 4, 5, 13-16, 18 and 19 was disclosed at the time the subject matter of those claims were made, under the provisions of 35 U.S.C. §102(b), based on the teachings of *Toshiyuki* (JP 10-424586).

VII. GROUPING OF CLAIMS:

Based on the rejection set forth by the Examiner, the claims 1, 2, 4, 5, 13-16, 18 and 19 stand or fall together.

VIII. ARGUMENT:

Claims 1, 2, 4, 5, 13-16, 18 and 19 are not anticipated under 35 U.S.C. §102(b) based on the teachings of *Toshiyuki*

A. The Claimed Invention

The claimed invention claims an insulating nitride layer formed as a buffer layer, such as a buffer layer in a semiconductor device, from a group III-V nitride compound semiconductor heavily doped mostly with cadmium. The present application contains two independent claims, namely claims 1 and 13.

Claim 1 claims an insulating nitride layer formed as a buffer layer from a group III-V nitride compound semiconductor heavily doped mostly with cadmium.

Claim 13 claims a semiconductor device which has an insulating nitride layer formed as a buffer layer from a group III-V nitride compound semiconductor heavily doped mostly with cadmium.

B. The Rejection

The Final Rejection rejects the pending claims as being allegedly anticipated by *Toshiyuki*. The Examiner argues that *Toshiyuki* teaches a buffer layer that is heavily doped mostly with cadmium. Since *Toshiyuki* is written in Japanese, the Examiner relies on two English-language translations of *Toshiyuki*. The first English-language translation is a Derwent English-language abstract ("the Derwent Abstract") of *Toshiyuki*, which is a three sentence summary of *Toshiyuki*. The other English-language translation is a Patent Abstracts of Japan ("the PAJ Abstract") computer-generated English-language translation of *Toshiyuki*.

To support the Examiner's argument that *Toshiyuki* discloses a buffer layer that is heavily doped mostly with cadmium, the Examiner relies on the three sentence Derwent Abstract. The Derwent Abstract states, in sentence 3, that cadmium is added to the buffer layer.

The Examiner also relies on the abstract and paragraphs [0011] and [0022] of the PAJ Abstract. However, those three passages of the PAJ Abstract clearly state that *Toshiyuki* has an AlGaInN layer adjacent its AlN buffer layer, and the AlGaInN layer is doped with a second impurity of cadmium, while there is no mention of the AlN buffer layer being doped with cadmium. The PAJ Abstract's abstract states, "an n-type AlGaInN layer adjacent to a buffer layer is doped with . . . second impurities comprising at least one of Mg, Ca, Zn, Cd, Hg, S or Se." (PAJ Abstract, abstract). Paragraph 0011 of the PAJ Abstract states, "[i]n the n type Al_xGa_{1-x-y}In_yN layer which adjoins the aforementioned buffer layer, . . . the 2nd impurity which consists of more of at least one of calcium (calcium), zinc (Zn), cadmium (Cd), mercury (Hg), sulfur (S), or selenium (Se) is added." (PAJ Abstract, paragraph [0011]). Paragraphs [0018] and [0022] of the PAJ Abstract disclose that a cadmium (Cd) impurity was used in "the GaN film on the AlN buffer layer." (PAJ Abstract, paragraphs [0018] and [0022]).

C. Toshiyuki Fails to Anticipate the Claimed Invention

Appellants submit that none of the claims are anticipated by *Toshiyuki*. *Toshiyuki* fails to disclose or even suggest features of the claimed invention, namely an insulating nitride layer formed as a buffer layer that is heavily doped mostly with cadmium.

1. The PAJ Abstract of *Toshiyuki* fails to teach doping a buffer layer with cadmium

The PAJ Abstract (which was provided to Appellants with the Final Rejection) clearly states repeatedly that *Toshiyuki* dopes an AlGaInN layer (or GaN layer), which is adjacent an AlN buffer layer, with cadmium. (PAJ Abstract, abstract, claim 1, [0011], [0018] with [0022], [0023] with [0024], [0026]).

Throughout the PAJ Abstract of *Toshiyuki*, the PAJ Abstract teaches forming an AlGaInN layer (or GaN layer) adjacent an AlN buffer layer, and doping that AlGaInN layer with cadmium. For example, in the abstract of the PAJ Abstract, it states that "an n-type AlGaInN layer adjacent to a buffer layer is doped with . . . second impurities comprising at least one of Mg, Ca, Zn, Cd, Hg, S or Se." (emphasis added) (PAJ Abstract, abstract). Paragraph 0011 of the PAJ Abstract states, "[i]n the n type Al_x Ga_{1-x-y} In_y N layer which adjoins the aforementioned buffer layer, . . . the 2nd impurity which consists of more of at least one of calcium (calcium), zinc (Zn), cadmium (Cd), mercury (Hg), sulfur (S), or selenium (Se) is added." (emphasis added) (PAJ Abstract, paragraph [0011]). Further, paragraphs [0018] and [0022] of the PAJ Abstract disclose that a cadmium (Cd) impurity was used in "the GaN film on the AlN buffer layer." (emphasis added) (PAJ Abstract, paragraphs [0018] and [0022]). These three passages from the PAJ Abstract clearly show that *Toshiyuki* teaches an AlGaInN layer (or GaN layer) formed on an AlN buffer layer, and that *Toshiyuki* dopes the AlGaInN layer with cadmium.

Contrary to the Examiner's assertion, none of the three above-described passages from the PAJ Abstract teach doping a buffer layer with cadmium. The Examiner argues that the abstract

and paragraphs [0011] and [0022] of the PAJ Abstract allegedly teach doping a buffer layer with cadmium. Appellants respectfully disagree with the Examiner. The relevant texts from those passages are reproduced above, and those passages clearly describe doping an AlGaInN layer adjacent a buffer layer with cadmium. Nowhere do the abstract or paragraphs [0011] and [0022] of the PAJ Abstract even describe doping a buffer layer. In fact, nowhere does the PAJ Abstract describe a buffer layer doped with cadmium.

2. **The Derwent Abstract of *Toshiyuki* is an incorrect English-language translation of *Toshiyuki***

In addition to the PAJ Abstract, the Examiner also provided an English-language Derwent Abstract of *Toshiyuki*, however, the Derwent Abstract is an incorrect English-language translation of *Toshiyuki*. The three sentence Derwent Abstract states that *Toshiyuki's* buffer layer is doped with cadmium. (Derwent Abstract, sentence 3). However, that translation contradicts with the PAJ Abstract translation of *Toshiyuki*. The PAJ Abstract, which is a translation of the complete text of *Toshiyuki*, repeatedly describes doping an AlGaInN layer adjacent a buffer layer with cadmium. (PAJ Abstract, abstract, claim 1, [0011], [0018] with [0022], [0023] with [0024], [0026]). While the three sentence Derwent Abstract mistakenly describes doping a buffer layer with cadmium. (Derwent Abstract, sentence 3).

Appellants respectfully submit that the PAJ Abstract is a more correct translation of *Toshiyuki* than the Derwent Abstract, and should therefore be relied on instead of the Derwent Abstract. As further evidence that the Derwent Abstract provides an incorrect translation, Appellants submit herewith a certified English-language translation of *Toshiyuki* ("the Certified Translation") in Appendix B. The Certified Translation tracks closely to the PAJ Abstract. Thus, similar to the PAJ Abstract, the Certified Translation also describes doping an AlGaInN layer adjacent a buffer layer with cadmium. (Certified Translation, solving means, claim 1, [0011], [0018] with [0022], [0023] with [0024], [0026]). Appellants note that the Certified Translation

describes doping the AlGaInN layer adjacent the buffer layer with cadmium at text locations that correspond to text locations in the PAJ Abstract. Nowhere does the Certified Translation even discuss a buffer layer doped with cadmium.

Therefore, the Derwent Abstract of *Toshiyuki* is an incorrect translation and should not be used. The PAJ Abstract of *Toshiyuki* is a more correct translation, as evidenced by the Certified Translation of *Toshiyuki* provided herewith. The PAJ Abstract and the Certified Translation of *Toshiyuki* clearly fail to disclose or even suggest a buffer layer doped with cadmium. Therefore, Appellants respectfully submit that *Toshiyuki* fails to anticipate independent claims 1 and 10.

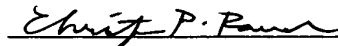
Further, claims 2, 4, 5, 14-16, 18 and 19 depend directly or indirectly from claims 1 or 13 and thus are allowable over *Toshiyuki* for at least the same reasons that claims 1 and 13 are allowable.

Accordingly, Appellants respectfully request that the Board reverse the rejection of the pending claims under 35 U.S.C. §102(b).

IX. CONCLUSION:

For the foregoing reasons, Appellants respectfully submit that the rejection posed by the Examiner is improper as a matter of law and fact. Accordingly, Appellants respectfully request the Board reverse the rejections of claims 1, 2, 4, 5, 13-16, 18 and 19 and allow claims 1, 2, 4, 5, 13-16, 18 and 19.

Respectfully submitted,

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APPENDIX A

1. (Previously presented) An insulating nitride layer formed as a buffer layer from a group III-V nitride compound semiconductor heavily doped mostly with cadmium.

2. (Previously presented) An insulating nitride layer as defined in Claim 1, which is heavily doped substantially with said cadmium as an impurity.

3. (Canceled).

4. (Previously presented) An insulating nitride layer as defined in Claim 1, which is doped with said cadmium in an amount not less than $1 \times 10^{17}/\text{cm}^3$.

5. (Original) An insulating nitride layer as defined in Claim 1, in which said group III-V nitride compound semiconductor is GaN, AlN, InN, or BN, or a mixture thereof.

6-12. (Withdrawn).

13. (Previously presented) A semiconductor device which has an insulating nitride layer formed as a buffer layer from a group III-V nitride compound semiconductor heavily doped mostly with cadmium.

14. (Original) A semiconductor device as defined in Claim 13, in which said group III-V nitride compound semiconductor

15. (Original) A semiconductor device as defined in Claim 13, in which an active layer is formed on said insulating nitride layer.

16. (Amended) A semiconductor device as defined in Claim 13, in which the insulating nitride layer is heavily doped substantially with said cadmium as an impurity.

17. (Canceled).

18. (Amended) A semiconductor device as defined in Claim 13, in which the insulating nitride layer is doped with said cadmium in an amount not less than $1 \times 10^{17}/\text{cm}^3$.

19. (Original) A semiconductor device as defined in claim 13 or 14, in which said group III-V nitride compound semiconductor is GaN, AlN, InN, or BN, or a mixture thereof.

20-27. (Withdrawn).

APPENDIX B

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

APPLICANTS: Fumihiko Nakamura

SERIAL NO.: 09/925,153 GROUP ART UNIT: 2813

FILING DATE: August 8, 2001 EXAMINER: BLUM, DAVID S

TITLE: Insulating nitride layer and process for its forming,
and semiconductor device and process for its productionHon. Commissioner of Patents and Trademarks,
Washington, D.C. 20231

S I R:


CERTIFIED TRANSLATION

I, Masaaki Iwami of 3-22, Asagaya-minami 1-chome, Suginami-ku, Tokyo, Japan, am an experienced translator of the Japanese language into the English language and I hereby certify that the attached comprises an accurate translation into English of Japanese Patent Laid-open No. Hei 10-242586 laid open September 11, 1998.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

February 20, 2004

Date


Masaaki IWAMI

Japanese Patent Laid-open No.: Hei 10-242586

Japanese Patent Laid-open Date: September 11, 1998

Japanese Patent Application No.: Hei 9-55590

Japanese Patent Application Date: February 24, 1997

Applicant: Fuji Electric Co., Ltd.

[Title of the Invention] GROUP III NITRIDE SEMICONDUCTOR
DEVICE AND METHOD OF MANUFACTURING THE SAME

[Abstract]

[Object] To provide a Group III nitride semiconductor device which has good crystallinity and a method of manufacturing a Group III nitride semiconductor device in which cracking is prevented.

[Solving Means] A Group III nitride semiconductor device includes a plurality of layers comprised of $\text{Al}_x\text{Ga}_{1-x-y}\text{In}_y\text{N}$ (where $0 \leq x \leq 1$, $0 \leq y \leq 1$, with $x = y = 0$ included) on a single-crystalline substrate, with a buffer layer comprised of GaN or AlN therebetween, wherein the $\text{Al}_x\text{Ga}_{1-x-y}\text{In}_y\text{N}$ layer adjacent to said buffer layer contains, added thereto, a first impurity including at least one selected from the group consisting of carbon (C), silicon (Si), germanium (Ge), and oxygen (O) and a second impurity including at least one selected from the group consisting of magnesium (Mg), calcium (Ca), zinc (Zn), cadmium (Cd), mercury (Hg), sulfur (S), and selenium (Se). Fig.1 shows SEM photographs of GaN films, in which (a) shows the case of simultaneous addition of Si and Mg, and (b) shows the case of addition of Si only.

[Claims]

[Claim 1] A Group III nitride semiconductor device comprising a plurality of layers comprised of $\text{Al}_x\text{Ga}_{1-x-y}\text{In}_y\text{N}$ (where $0 \leq x \leq 1$, $0 \leq y \leq 1$, with $x = y = 0$ included) on a single-crystalline substrate, with a buffer layer comprised of GaN or AlN therebetween, wherein an n-type $\text{Al}_x\text{Ga}_{1-x-y}\text{In}_y\text{N}$ layer adjacent to said buffer layer contains, added thereto, a first impurity comprising at least one selected from the group consisting of carbon (C), silicon (Si), germanium (Ge), and oxygen (O) and a second impurity comprising at least one selected from the group consisting of magnesium (Mg), calcium (Ca), zinc (Zn), cadmium (Cd), mercury (Hg), sulfur (S), and selenium (Se).

[Claim 2] A Group III nitride semiconductor device as set forth in claim 1, wherein the concentration of said first impurity is from 1×10^{17} to $2 \times 10^{19} \text{ cm}^{-3}$, and the concentration of said second impurity is from 1×10^{15} to $2 \times 10^{17} \text{ cm}^{-3}$.

[Claim 3] A Group III nitride semiconductor device as set forth in claim 1 or 2, wherein said substrate is comprised of a single crystal of silicon, germanium, or silicon carbide.

[Claim 4] A Group III nitride semiconductor device as set forth in any of claims 1 to 3, wherein said Group III

nitride semiconductor device is a light-emitting device comprising an n-type clad layer, an active layer, and a p-type clad layer, such as a light-emitting diode and a laser diode, and said n-type clad layer is said n-type $\text{Al}_x\text{Ga}_{1-x-y}\text{In}_y\text{N}$ layer.

[Claim 5] A method of manufacturing a Group III nitride semiconductor device set forth in any of claims 1 to 4, wherein the film of said $\text{Al}_x\text{Ga}_{1-x-y}\text{In}_y\text{N}$ is conducted by molecular beam epitaxy.

[Claim 6] A method of manufacturing a Group III nitride semiconductor device as set forth in claim 6, wherein silicon (Si) and germanium (Ge) of said first impurity as well as said second impurity are supplied from effusion cells.

[Claim 7] A method of manufacturing a Group III nitride semiconductor device as set forth in claim 6, wherein said carbon (C) is evaporated by irradiation with electron beams.

[Claim 8] A method of manufacturing a Group III nitride semiconductor device as set forth in claim 6, wherein said oxygen (O) is introduced into a radical generation source of a high-frequency excitation type which is the same as that for the raw material nitrogen (N) of the Group III nitride.

[Detailed Description of the Invention]

[0001]

[Technical Field of the Invention] The present invention relates to a Group III nitride semiconductor device including an $\text{Al}_x\text{Ga}_{1-x-y}\text{In}_y\text{N}$ ($0 \leq x, y$ and $x+y \leq 1$) based semiconductor thin film laminated on a substrate, such as a light-emitting device, and a method of manufacturing the same.

[0002]

[Prior Art] Hitherto, Group III nitride semiconductor devices, such as semiconductor lasers and light-emitting diodes, which use an $\text{Al}_x\text{Ga}_y\text{In}_{1-x-y}\text{N}$ ($0 \leq x, y$ and $x+y \leq 1$) based material of the direct transition type with an optical energy gap controllable in the range of 1.9 to 6.2 eV, have been produced on a test basis. Since it has not been made possible to produce a large single crystal of GaN or AlN, in the above-mentioned Group III nitride semiconductor devices, mainly sapphire (Al_2O_3), spinel (MgAl_2O_4) and the like have been widely used as a substrate, although they are not necessarily good in matching performance of lattice and coefficient of thermal expansion. In this case, it has become possible to control n-type and p-type valence electrons by adding

silicon (Si) and/or magnesium (Mg), and to control the optical energy gap by varying the values of x and y in the formula $\text{Al}_x\text{Ga}_y\text{In}_{1-x-y}\text{N}$ (which may hereinafter be abridged to AlGaInN).

[0003] A few examples of the recent Group III nitride semiconductor devices will be mentioned. Fig. 6 is a sectional view of a light-emitting device of the double hetero (DH) structure which is the simplest in the prior art (S. Nakamura et al, Japanese Journal of Applied Physics, vol. 32 (1993), L8-L11). First, a buffer layer 2 comprised of a film of low-temperature GaN formed at a low temperature of 400 to 500 °C is formed on a sapphire substrate 1 with a substrate surface being (0001) plane. Thereafter, a first clad layer 4 functioning also as a base layer of 3000 nm in thickness comprised of n-type GaN, an active layer 5 of 20 nm in thickness comprised of p-type GaInN, and a second clad layer 6 comprised of p-type GaN are sequentially laminated at a high temperature of about 1000 °C. A p-side electrode layer 7a is formed on the second clad layer 6. Since the sapphire substrate 1 is an insulator, parts of the active layer 5 to the second clad layer 6 are removed by etching or the like, and an n-side electrode layer 7b is formed on the exposed first clad layer 4. The four side surfaces of the etched

or cut active layer are light output surfaces.

[0004] Fig. 7 is a sectional view of a laser diode of the multiple quantum well (MQW) structure according to the prior art (S. Nakamura et al, Japanese Journal of Applied Physics, vol. 32 (1993), L74-L76). The substrate surface of a substrate 1 is (0001) plane of sapphire. First, a buffer layer 2 comprised of n-type GaN is formed as a first layer. Thereafter, a base layer 3 comprised of n-type GaN, a crack inhibitive layer 3a comprised of n-type InGa_N, a first clad layer 4 comprised of n-type AlGa_N, a light guide layer 4a comprised of n-type GaN, an active layer 5q of the multiple quantum well structure comprised of p-type GaInN, a decomposition inhibitive layer 6b comprised of p-type AlGa_N, a light guide layer 6a comprised of p-type GaN, a second clad layer 6 comprised of p-type GaN, and a contact layer 7 comprised of p-type GaN are sequentially laminated. A p-side electrode layer 8a comprised of Au/Cr is formed on the contact layer 7, and an n-side electrode layer 8b comprised of Al is formed on the back side of the substrate.

[0005] In each of the cases, a buffer layer is formed on a substrate, and then a base layer is formed to be thick, in order to enhance crystallinity of the base layer.

[0006]

[Problems to Be Solved by the Invention] In general, it is known that, where a c-axis orientated film of a material having a hexagonal structure is formed or grown on a substrate, the rate of growth on the substrate is not uniform in all directions and there is a tendency toward three-dimensional growth (island form growth). The same fact is observed also in the case of $\text{Al}_x\text{Ga}_y\text{In}_{1-x-y}\text{N}$ which is a hexagonal crystal. In such a film, the surface is very largely rugged and crystallinity is poor. In order to obviate this problem, an AlN film comparatively low in the tendency or a GaN film grown at a low temperature may be used as a buffer layer, whereby the growth in a-axis direction is promoted to some extent, and a film good in surface flatness and crystallinity is obtained. However, it is also reported that the film obtained by use of the buffer layer is not yet sufficient in terms of film quality for application to a laser diode and that, when a large current is injected, the electrode material will diffuse along the grain boundaries arising from the island form growth (the grain boundaries which are the interfaces of collision of grown islands). Therefore, in order to obtain a good-quality laser diode, it is necessary to further promote the growth in the a-axis direction.

[0007] In addition, AlGaIn is higher than the GaN film in tendency toward three-dimensional growth, and, therefore, the growth of an AlGaIn clad layer is conducted on two layers, i.e., a thin buffer layer and a base layer comprised of GaN having a large thickness of 1 μm or more which are formed on the substrate, for the purpose of enhancing crystallinity. In the second prior art example (Fig. 6), a GaInN layer 100 nm in thickness is further formed on the base layer as a crack inhibitive layer.

[0008] However, where a substrate lower than a GaAlInN based material in coefficient of thermal expansion is used, or where a substrate lower than the GaAlInN based material in lattice constant is used, a tensile stress is generated in the GaAlInN film, and, depending on the total thickness of the AlGaInN film, crack may be generated in the film. For example, where an AlN buffer layer was formed in a thickness of 6 nm on an Si (111) substrate and a GaAlInN film was formed thereon, a crack was observed when the thickness of the GaAlInN film reached or exceeded 1.5 μm . In the case of producing a laser diode, in order to obtain a light confining effect, it is necessary to provide a clad layer with a thickness of about 500 nm, and, since the DH structure includes an active layer sandwiched between two n-type and p-type

clad layers, even a setting of the thickness of the active layer to about 50 nm results in that the total thickness of the clad layers and the active layer is 1050 nm. In an actual device structure, furthermore, the above-mentioned GaN layer is provided beneath the n-type clad layer, and a p-type GaN is formed on the p-type clad layer in order to improve the contact of an electrode with the p-type; as a result, the total film thickness is close to 3 μ m. With such a film thickness, a crack is surely generated where an Si substrate is used.

[0009] One of the methods for restraining the generation of a crack resides in setting the film thickness of the semiconductor device to be small. If an n-type clad layer can be formed directly on the thin buffer layer formed on the substrate, it is possible to prevent cracking. In order to form the n-type clad layer directly on the buffer layer, it is necessary to restrain the three-dimensional growth (island form growth) and to promote two-dimensional growth (growth in the a-axis direction) by some method.

[0010] It is an object of the present invention to provide a Group III nitride semiconductor device having good crystallinity, and a method of manufacturing a Group III nitride semiconductor device in which cracking is

prevented.

[0011]

[Means for Solving the Problems] In order to attain the above object, according to the present invention, there is provided a Group III nitride semiconductor device comprising a plurality of layers comprised of $\text{Al}_x\text{Ga}_{1-x-y}\text{In}_y\text{N}$ (where $0 \leq x \leq 1$, $0 \leq y \leq 1$, with $x = y = 0$ included) on a single-crystalline substrate, with a buffer layer comprised of GaN or AlN therebetween, wherein an n-type $\text{Al}_x\text{Ga}_{1-x-y}\text{In}_y\text{N}$ layer adjacent to the buffer layer contains, added thereto, a first impurity comprising at least one selected from the group consisting of carbon (C), silicon (Si), germanium (Ge), and oxygen (O) and a second impurity comprising at least one selected from the group consisting of magnesium (Mg), calcium (Ca), zinc (Zn), cadmium (Cd), mercury (Hg), sulfur (S), and selenium (Se).

[0012] Preferably, the concentration of the first impurity is preferably from 1×10^{17} to $2 \times 10^{19} \text{ cm}^{-3}$, and the concentration of the first impurity is from 1×10^{15} to $2 \times 10^{17} \text{ cm}^{-3}$. The substrate is preferably comprised of a single crystal of silicon, germanium, or silicon carbide. Here, where the single-crystalline substrate itself is used as an electrode, the carrier concentration in the substrate is preferably controlled to within the range of

10^{18} to 10^{20} cm^{-3} , in order to reduce the resistance thereof.

[0013] Preferably, the Group III nitride semiconductor device is a light-emitting device comprising an n-type clad layer, an active layer, and a p-type clad layer, such as a light-emitting diode and a laser diode, and the n-type clad layer is the above-mentioned n-type $\text{Al}_x\text{Ga}_{1-x-y}\text{In}_y\text{N}$ layer. In a method of manufacturing a Group III nitride semiconductor device as above-mentioned, the film of $\text{Al}_x\text{Ga}_{1-x-y}\text{In}_y\text{N}$ is formed by molecular beam epitaxy.

[0014] Silicon (Si) and germanium (Ge) of the first impurity as well as the second impurity are preferably supplied from effusion cells. Carbon (C) is preferably evaporated by irradiation with electron beams. Oxygen (O) is preferably introduced into a radical generation source of the high-frequency excitation type which is the same as that for the raw material nitrogen (N) of the Group III nitride.

[0015]

[Mode for Carrying Out the Invention] It has been reported, based on a simulation relating to the growth of GaN, particularly to the relationship between flux quantities of Ga and N supplied to a substrate and the crystal surface of a crystal being grown and the

mechanism of crystal growth, that two-dimensional growth performance is promoted where the Ga flux quantity is larger than the N flux quantity (K. Wang et al, Journal Applied Physics vol. 76 (1994), 3502-3510). This is explained as follows. In consideration of migration of particles on the substrate at a fixed substrate temperature, non-polar Ga elementary particles are less influenced by the substrate surface and the crystal surface of the crystal being grown and, therefore, lead to easier migration, as compared with particles of polar GaN molecules.

[0016] When the Ga flux quantity is excessively large, however, Ga would be crystallized on the film surface in the state of Ga metal. The present invention is based on a finding that, when a metal with such a high vapor pressure as not to be crystallized on the film due to re-evaporation even if excessively supplied and, further, another metal not generating defects in the crystal even if taken into the film are flux-supplied simultaneously with Ga, it is possible to prevent crystallization of Ga and to promote the two-dimensional growth performance. In addition, such a crystal growth situation applies also to AlN, InN, and a mixed crystal thereof (AlGaInN), which are comprised of the same group elements as those of GaN

and have the same crystal structure as that of GaN.

[0017] As an element satisfying the above two conditions, there may be considered magnesium (Mg), calcium (Ca), zinc (Zn), cadmium (Cd), mercury (Hg), sulfur (S), and selenium (Se). Fig. 5 is a graph showing the temperature dependence of the vapor pressures of the additive elements (R.E. Honig and D.A. Kramer, RCA Review, vol. 30, 285 (1969)). In the vicinity of 800 °C at which the film of the AlGaInN based material is to be formed, the vapor pressures of these elements are higher than that of Ga by 10^4 or more, so that even if the particles of these elements reach the substrate, most of the particles are re-evaporated. Besides, it is considered that, even if these elements are mixed into the AlGaInN based film in small amounts, the crystallinity of the mother material would not be degraded, since Mg, Ca, Zn, Cd, and Hg undergo substitution at Ga sites to function as acceptors whereas S and Se function as donors.

Example 1:

As Example 1 of the present invention, a GaN film with Si and Mg added thereto was formed on an Si (111) plane substrate, with an AlN buffer therebetween. The film was formed by a molecular beam epitaxy (MBE) method in which Al metal, Ga metal, Si, and Mg metal as starting

materials were fed respectively into separate effusion cells, and were heated to obtain respective metal vapor fluxes. Besides, a nitrogen radical flux was obtained by use of a nitrogen radical generation source of the high-frequency excitation type. First, the Al vapor flux and the nitrogen radical flux were radiated onto the Si (111) plane substrate, to form an AlN buffer layer with a film thickness of about 6 nm. The substrate temperature was 840 °C. Next, shutters of Ga, Si, and Mg effusion cells were opened simultaneously, and the vapor fluxes of these elements were radiated simultaneously with the nitrogen radical flux, to form a GaN film with Si and Mg added thereto. The substrate temperature was 840 °C, the same as that for the AlN buffer layer, and the Ga, Si, and Mg cell temperatures were 1080 °C, 1150 °C, and 420 °C, respectively. For comparison, a conventional GaN film without Mg added thereto was also formed. In each of the cases, the GaN film thickness was set to 670 nm.

[0018] Fig. 1 shows microphotographs (SEM photographs) showing a section of the GaN film on the AlN buffer layer according to the present invention, in which (a) shows the case of addition of both Mg and Si according to the present invention, and (b) shows the case of addition of only Si according to the prior art. The surface of the

GaN film is rugged in (b), but is flat in (a), which shows that by adding Si and Mg simultaneously, the growth in the a-axis direction is promoted, resulting in a flat film surface. These films were subjected to measurement of half-width of rocking curve of (0001) plane by X-ray diffraction, upon which it was found that the half-width in the case of film growth without Mg addition is 15 min, while the half-width in the case of film growth with Mg addition is 7 min. Thus, it was confirmed that the addition of Mg enhanced crystallinity even when the film thickness was less than 1 μm .

[0019] Besides, as a result of composition analysis by SIMS, it was found that the Si concentration in the film was $2 \times 10^{19} \text{ cm}^{-3}$, whereas the Mg concentration in the film was $2 \times 10^{17} \text{ cm}^{-3}$. In addition, as a result of carrier concentration measurement by Hall measurement, the films were found to be n-type irrespective of the presence or absence of Mg addition, and the carrier concentration was found to be about $2 \times 10^{19} \text{ cm}^{-3}$. Further, an experiment was conducted in which the Si concentration was varied while the Mg concentration was fixed at 1% based on the Si concentration. In the Si concentration range of 1×10^{17} to $2 \times 10^{19} \text{ cm}^{-3}$, the enhancement of film quality by the Mg addition as above-mentioned was observed.

[0020] Besides, an experiment was conducted in which only the Mg concentration was varied. When the Mg concentration exceeded $2 \times 10^{17} \text{ cm}^{-3}$, electron mobility was lowered. When the Mg concentration was less than $2 \times 10^{15} \text{ cm}^{-3}$, a conspicuous enhancement of film quality by the Mg addition was not observed.

Example 2:

By use of carbon (C) in place of Si as a donor impurity, a GaN film with Mg and C simultaneously added thereto was formed. Incidentally, carbon was heated and evaporated by irradiation with electron beams. Where C was thus used as the donor impurity, also, an enhancement of GaN film quality by Mg addition was observed in an Mg concentration range of 2×10^{15} to $2 \times 10^{17} \text{ cm}^{-3}$, in the same manner as in the case of Si in Example 1.

[0021] Besides, when the Mg concentration exceeded $2 \times 10^{17} \text{ cm}^{-3}$, electron mobility was lowered, and, when the Mg concentration was less than $2 \times 10^{15} \text{ cm}^{-3}$, a conspicuous enhancement of film quality by Mg addition was not observed.

Example 3:

By use of germanium (Ge) in place of Si as a donor impurity, a GaN film with Mg and C simultaneously added thereto was formed. Incidentally, Ge was heated by use of

an effusion cell, in the same manner as in the case of Si. Where Ge was thus used as the donor impurity, also, an enhancement of GaN film quality by Mg addition was observed in an Mg concentration range of 2×10^{15} to 2×10^{17} cm^{-3} , in the same manner as in the case of Si. Besides, when the Mg concentration was less than 2×10^{15} cm^{-3} , a conspicuous enhancement of film quality by Mg addition was not observed.

[0022] In addition, when the Mg concentration exceeded 2×10^{17} cm^{-3} , electron mobility was lowered, and, when the Mg concentration was less than 2×10^{15} cm^{-3} , a conspicuous enhancement of film quality by Mg addition was not observed.

Example 4:

By use of oxygen (O) in place of Si as a donor impurity, a GaN film with Mg and C simultaneously added thereto was formed. Incidentally, oxygen was introduced into a nitrogen radical generation source through a flow meter, and was radiated to the film as oxygen radicals together with nitrogen radicals. Where oxygen was thus used as the donor impurity, also, an enhancement of GaN film quality by Mg addition was observed in an Mg concentration range of 2×10^{15} to 2×10^{17} cm^{-3} , in the same manner as in the case of Si.

Example 5:

By use of calcium (Ca) in place of Mg, a GaN film with Ca and Si simultaneously added thereto was produced. Where Ca was thus used, also, an enhancement of film quality by Ca addition was observed in a Ca concentration range of 2×10^{15} to $2 \times 10^{17} \text{ cm}^{-3}$, in the same manner as in the case of Mg.

Example 6:

By use of zinc (Zn) in place of Mg, a GaN film with Zn and Si simultaneously added thereto was formed. Where Zn was thus used, also, an enhancement of film quality by Zn addition was observed in a Zn concentration range of 2×10^{15} to $2 \times 10^{17} \text{ cm}^{-3}$, in the same manner as in the case of Mg.

Example 7:

By use of cadmium (Cd) in place of Mg, a GaN film with Cd and Si simultaneously added thereto was produced. Where Cd was thus used, also, an enhancement of film quality by Cd addition was observed in a Cd concentration range of 2×10^{15} to $2 \times 10^{17} \text{ cm}^{-3}$, in the same manner as in the case of Mg.

Example 8:

By use of mercury (Hg) in place of Mg, a GaN film with Hg and Si simultaneously added thereto was formed. Where

Hg was thus used, also, an enhancement of film quality by Hg addition was observed in an Hg concentration range of 2×10^{15} to $2 \times 10^{17} \text{ cm}^{-3}$, in the same manner as in the case of Mg.

Example 9:

By use of sulfur (S) in place of Mg, a GaN film with S and Si simultaneously added thereto was formed. Where S was thus used, also, an enhancement of film quality by S addition was observed in an S concentration range of 2×10^{15} to $2 \times 10^{17} \text{ cm}^{-3}$, in the same manner as in the case of Mg.

Example 10:

By use of selenium (Se) in place of Mg, a GaN film with Se and Si simultaneously added thereto was formed. Where S was thus used, also, an enhancement of film quality by Se addition was observed in an Se concentration range of 2×10^{15} to $2 \times 10^{17} \text{ cm}^{-3}$, in the same manner as in the case of Mg.

Example 11:

In this example, an $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ film which is an n-type clad material was formed, in the same manner as the GaN film in Example 1.

[0023] Fig. 3 is a microphotograph (SEM photograph) showing a section of an AlGaIn film on an AlN buffer layer

according to the prior art. The $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ film is higher than the GaN film in tendency to grow in an island form, and, when it is directly formed on an AlN buffer layer on an Si (111) plane substrate, a severely rugged film is obtained, as shown in Fig. 3. In order to obviate the ruggedness, it has been a common practice to first build up GaN on the AlN buffer layer and then form the $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ film thereon, as has been described above as an example of the prior art. It was found out, however, that when Mg in a concentration of 1×10^{15} to $2 \times 10^{17} \text{ cm}^{-3}$ is added simultaneously with a donor impurity such as Si, the crystallinity-enhancing effect obtained in the case of the GaN film can be attained also in the case of the $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ film. Fig. 2 is a microphotograph (SEM photograph) showing a section of an AlGaIn film with Si and Mg simultaneously added thereto according to the present invention. It is seen that the surface of the AlGaIn film is free of severe ruggedness and is extremely flat.

[0024] This effect was obtained not only in the case of Si, as in Example 1, but also in the cases of C, Ge and O, used in combination with calcium (Ca), zinc (Zn), cadmium (Cd), mercury (Hg), sulfur (S), or selenium (Se). Based on the results, the following laser diode was produced on

a test basis. Fig. 4 is a sectional view of a laser diode of the DH structure using an AlGaInN film with Si and Mg simultaneously added thereto according to the present invention. An AlN buffer layer 2 with a film thickness of 6 nm was formed on an n-type Si (111) substrate 1, and then a first clad layer 4 with a thickness of 500 nm comprised of an n-type $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ with Si and Mg simultaneously added thereto, an active layer 5 with a thickness of 50 nm comprised of GaN without addition of any additive element, a second clad layer 6 with a thickness of 500 nm comprised of p-type $\text{Al}_{0.2}\text{Ga}_{0.8}\text{N}$ with only Mg added thereto, and a contact layer 7 with a thickness of 100 nm comprised of p-type GaN with only Mg added thereto, were laminated thereon. Then, a p-side electrode 8a of Cr/Au was formed on the contact layer 7, whereas an n-side electrode 8b of Al was formed on the back side of the substrate 1. By cleaving the (111) plane of the Si substrate, the (1-100) plane of the AlGaInN material was cleaved, and the cleaved plane was used as an optical resonance plane of an optical resonator. In this DH device, it was possible to omit a GaN layer, which has been required in the prior art; therefore, the total film thickness was as small as 1150 nm, and no crack was generated in the film.

[0025] When a pulsed current was passed from the p-type GaN to the Si (111) substrate at room temperature, laser oscillation was observed at a current value of 800 mA or more.

Example 12:

By use of an n-type Ge (111) or SiC (0001) plane in place of the Si (111) substrate in Example 11, the same DH structure as in Example 11 was produced, and the same results as above were obtained.

[0026]

[Effects of the Invention] According to the present invention, there is provided a Group III nitride semiconductor device comprising a plurality of layers comprised of $\text{Al}_x\text{Ga}_{1-x-y}\text{In}_y\text{N}$ (where $0 \leq x \leq 1$, $0 \leq y \leq 1$, with $x = y = 0$ included) on a single-crystalline substrate, with a buffer layer comprised of GaN or AlN therebetween, wherein the $\text{Al}_x\text{Ga}_{1-x-y}\text{In}_y\text{N}$ layer adjacent to said buffer layer contains, added thereto, a first impurity comprising at least one selected from the group consisting of carbon (C), silicon (Si), germanium (Ge), and oxygen (O) and a second impurity comprising at least one selected from the group consisting of magnesium (Mg), calcium (Ca), zinc (Zn), cadmium (Cd), mercury (Hg), sulfur (S), and selenium (Se). Therefore, the

crystallinity and morphology of the film are enhanced, and it is possible to obtain a Group III nitride semiconductor device, such as an LED and a semiconductor laser, which has high quality.

[Brief Description of the Drawings]

[Fig. 1] Fig. 1 shows microphotographs (SEM photographs) showing a section of a GaN film on an AlN buffer layer according to the present invention, in which (a) shows the case of addition of both Mg and Si according to the present invention, and (b) shows the case of addition of only Si according to the prior art;

[Fig. 2] Fig. 2 is a microphotograph (SEM photograph) showing a section of an AlGaIn film with Si and Mg simultaneously added thereto according to the present invention;

[Fig. 3] Fig. 3 is a microphotograph (SEM photograph) showing a section of an AlGaIn film on an AlN buffer layer according to the prior art;

[Fig. 4] Fig. 4 is a sectional view of a laser diode of the DH structure using an AlGaIn film with Si and Mg simultaneously added thereto according to the present invention;

[Fig. 5] Fig. 5 is a graph showing the temperature dependence of the vapor pressures of additive elements;

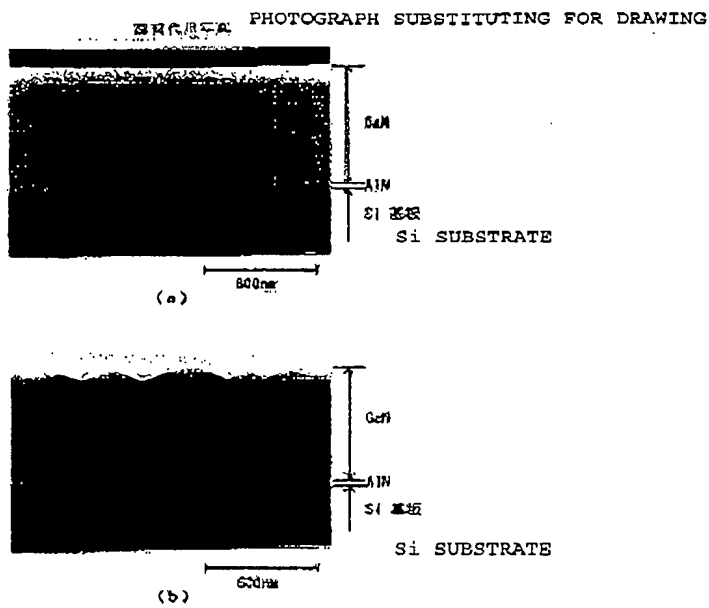
[Fig. 6] Fig. 6 is a sectional view of a light-emitting device of the simplest double hetero (DH) structure according to the prior art; and

[Fig. 7] Fig. 7 is a sectional view of a laser diode of the multiple quantum well (MQW) structure according to the prior art.

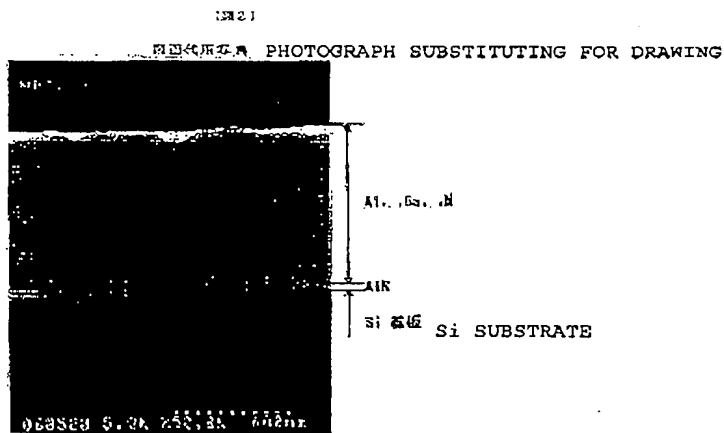
[Explanation of Symbols]

- 1: substrate
- 2: buffer layer
- 3: base layer
- 3a: crack inhibitive layer
- 4: first clad layer
- 4a: first light guide layer
- 5: active layer
- 6: second clad layer
- 6a: second light guide layer
- 6b: decomposition inhibitive layer
- 7: contact layer
- 8a: p-side electrode
- 8b: n-side electrode

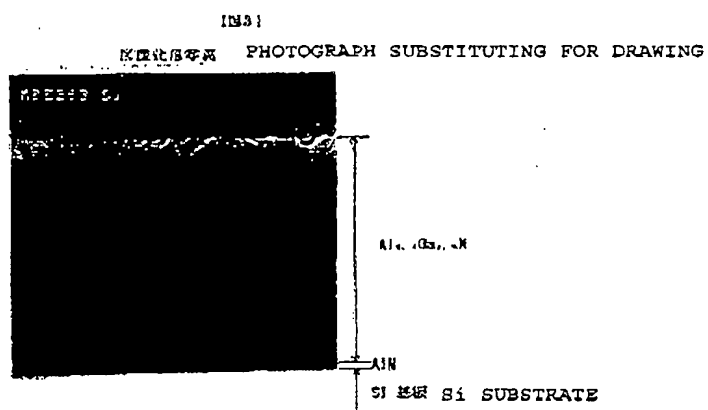
[FIG. 1]



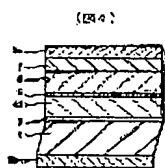
[FIG. 2]



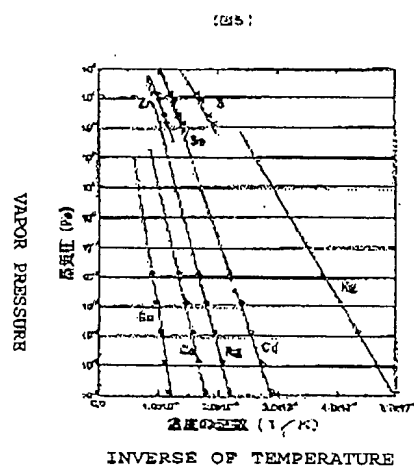
[FIG. 3]



[FIG. 4]

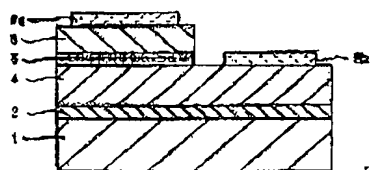


[FIG. 5]



[FIG. 6]

【図6】



[FIG. 7]

【図7】

